

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing:

06 July 2000 (06.07.00)

International application No.:

PCT/US99/29225

Applicant's or agent's file reference:

DeLiso 11

International filing date:

09 December 1999 (09.12.99)

Priority date:

30 December 1998 (30.12.98)

Applicant:

DELISO, Evelyn, M. et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International preliminary Examining Authority on:

01 May 2000 (01.05.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

J. Zahra

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 24 APR 2001

14 PCT

Applicant's or agent's file reference DELISO 11	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US99/29225	International filing date (day/month/year) 09 DECEMBER 1999	Priority date (day/month/year) 30 DECEMBER 1998
International Patent Classification (IPC) or national classification and IPC IPC(7): C03B 37/018 and US Cl.: 65/413, 384, 379		
Applicant CORNING INCORPORATED		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets.
☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 01 MAY 2000	Date of completion of this report 13 MARCH 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer JOHN HOFFMANN DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/29225

1. Basis of the report

1. With regard to the elements of the international application:*

☒ the international application as originally filed☒ the description:

pages 1-12 as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

☒ the claims:

pages 13-16, as originally filed
pages NONE, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of

☒ the drawings:

pages 1-8, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

☒ the sequence listing part of the description:

pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages NONE
☒ the claims, Nos. NONE
☒ the drawings, sheets/fig. NONE

5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

**Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/29225

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. statement**

Novelty (N)	Claims <u>1-16, 22-23</u>	YES
	Claims <u>17-21</u>	NO
Inventive Step (IS)	Claims <u>1-16</u>	YES
	Claims <u>17-23</u>	NO
Industrial Applicability (IA)	Claims <u>1-23</u>	YES
	Claims <u>NONE</u>	NO

2. citations and explanations (Rule 70.7)

Claims 1-16 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest creating a tantalum-doped preform by using as soot preform. XP-002141764 teaches using a gel body. There seems to be no motivation to make such via a soot technique.

Claims 17-21 lack novelty under PCT Article 33(2) as being anticipated by XP-002141764.

Claims 17-21 are very broad and are open to any and all impurities that could be found in the prior art gel-based glass. Thus one looking at the prior art glass body, one could not conclude that it was not made by the claimed method. Thus the XP-002141764 glass is indistinguishable from the claimed glass.

Claims 22-23 lack an inventive step under PCT Article 33(3) as being obvious over XP-002141764.

These two claims limit the optical characteristics. It would have been obvious to perform the prior art method so as to minimize the attenuation so as to reduce the number of repeaters.

----- NEW CITATIONS -----

NONE

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US99/29225

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C03B 37/014, 13/04, C03C 3/06	A2	(11) International Publication Number: WO 00/39039 (43) International Publication Date: 6 July 2000 (06.07.00)
(21) International Application Number: PCT/US99/29225 (22) International Filing Date: 9 December 1999 (09.12.99) (30) Priority Data: 60/114,369 30 December 1998 (30.12.98) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; One Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): DELISO, Evelyn, M. [US/US]; 248 Chemung Street, Corning, NY 14830 (US). MARLATT, Deborah, L. [US/US]; 898 County Route 85, Addison, NY 14801 (US). PIERSON, Michelle, D. [US/US]; 678 Beartown Road, Painted Post, NY 14870 (US). TENNENT, Christine, L. [US/US]; 4748 Clawson Drive, Campbell, NY 14821 (US). (74) Agent: CHERVENAK, William, J.; Corning Incorporated, Patent Dept., SP TI 3-1, Corning, NY 14831 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: TANTALA DOPED WAVEGUIDE AND METHOD OF MANUFACTURE		
(57) Abstract <p>The present invention is directed to low loss optical waveguides doped with tantala and methods for manufacturing such waveguides. SiO₂ soot is doped with Ta₂O₅ to form a soot blank which is consolidated under conditions suitable to prevent the crystallization within the Ta₂O₅-SiO₂ containing waveguides. The resulting cane is then either drawn into an optical fiber or overclad and subsequently drawn into an optical fiber. High temperature consolidation in either a gaseous atmosphere or vacuum atmosphere is used to sinter and vitrify the soot blank prior to drawing to produce a low loss optical waveguide fiber.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TANTALA DOPED WAVEGUIDE AND METHOD OF MANUFACTURE

FIELD OF THE INVENTION

5 The present invention relates generally to optical waveguide glass having a high index of refraction and a method for manufacturing such optical waveguide glass, and more particularly to a method of doping optical waveguide glass with Ta₂O₅ to produce essentially crystalline free optical waveguide fiber.

10 While the invention is capable of being carried out using a number of sput collection and doping techniques, it is particularly well suited for use in conjunction with the outside vapor deposition (OVD) process, and will be particularly described in that regard.

BACKGROUND OF THE INVENTION

15 In the rapidly expanding field of telecommunications, there is an ever-increasing demand for systems that transfer greater amounts of data in shorter periods of time. Accordingly, in the opto-electronics field, there is a continuing
20 need for new optical waveguide systems, and consequently new optical waveguides and new optical waveguide components for meeting the demands of those systems.

Generally speaking, optical waveguide fibers include a core surrounded by a cladding material having a refractive index lower than that of the core. Such optical waveguide fibers are generally composed of silica that is selectively doped with a dopant such as germanium. Although germanium is the principal and most widely used dopant, other dopants such as phosphorous, fluorine, boron and erbium, to name a few, are often used. Germania, however, is most commonly used due to its low melting point and high refractive index in relation to silica.

All dopants, including germania have shortcomings that limit their usefulness to certain applications. Accordingly, as technology improves and the requirements for new applications increases, the requirement for new optical waveguide fiber capable of meeting the demands of these applications increases as well. Such needs provide the incentive to consider the application of new dopants and new methods of doping optical waveguide fibers to meet these demands. In addition, competition is continually driving researchers to develop optical waveguide fibers at lower cost. Because germania costs approximately \$1,000 per kilogram, a less expensive dopant capable of providing a higher index of refraction than germania with less of that alternative dopant would be ideal.

One such dopant known to have a high refractive index is tantala. In fact, Ta_2O_5 thin films are widely used in thin-film waveguide lenses and anti-reflective coatings for silicon wafer solar cells. Because of the attractiveness of Ta_2O_5 , thin films for integrated optical devices, many researchers have been active in this area. Thin films for integrated optical devices containing Ta_2O_5 are typically fabricated using sputtering techniques and result in measurable losses of about 0.4 dB/cm. In the field of thin-films it is believed that a contributing factor to such high losses is the subsequent heat treatment of thin-films following sputtering. It was found that the heat treatment caused the film to change from amorphous to crystalline. Such a defect, if formed in an optical waveguide fiber, would adversely affect that optical waveguide fiber operating properties and would render the fiber non-functional in an optical waveguide fiber system.

Planar devices have also been fabricated using Ta_2O_5 . Ta_2O_5 - SiO_2 core glass for such devices is laid down using an electron beam vapor deposition technique. However, the lowest loss observed for such devices has been approximately 0.15 dB/cm or 15,000 dB/km. For optical waveguide fiber, losses of less than approximately 1 dB/km is the target. Thus, neither the thin-films nor the planar optical devices suggest the usefulness of tantala doped silica for optical waveguide fibers.

In view of the foregoing, there is a need for a dopant that, in limited quantities, is capable of providing a high core index of refraction to an optical waveguide fiber. In addition, there exists a need for a dopant that has good non-linear properties, does not adversely impact the mechanical properties of the optical waveguide fiber in which it resides, and exhibits beneficial amplification characteristics. Moreover, there is a need for a method of providing the dopant to an optical waveguide fiber with minimal deviation from present optical fiber manufacturing techniques, thus making it economically feasible and desirable. The low cost of tantala compared to germania, as well as tantala's high index of refraction makes it a promising candidate for such a dopant.

SUMMARY OF THE INVENTION

One aspect of the present invention relates to a method of manufacturing a low loss optical waveguide having a high refractive index core by forming a soot blank which includes Ta_2O_5 and SiO_2 , consolidating the soot blank to form a cane under conditions suitable to prevent crystallization of the Ta_2O_5 - SiO_2 containing glass and drawing the cane into an optical fiber.

In another aspect, the invention relates to an optical fiber that is manufactured by preparing a soot blank which includes at least Ta_2O_5 and SiO_2 , consolidating the soot blank to form a cane under conditions suitable to prevent crystallization of the Ta_2O_5 - SiO_2 containing glass and drawing the cane into an optical fiber.

A further aspect of the invention relates to an optical fiber having a high purity glass cladding, and a high refractive index glass core bounded by the cladding. The glass core includes between about 2 to 5 wt% Ta_2O_5 , so that light attenuation in the optical fiber is less than about 1.8 dB/km at 1550 nm.

5 Yet another aspect of the invention relates to a glass for use in the core of the optical waveguide that includes SiO_2 and, by weight on an oxide basis, between about 2% non-crystallized Ta_2O_5 , to 5% non-crystallized Ta_2O_5 after consolidation.

10 The glass and method of the present invention results in a number of advantages over other glasses and methods known in the art. One of the most attractive features of using tantalum in the glass for the present invention is its high index of refraction, which is reported to be 2.2 at 632.8 nm. Accordingly, in the glass of the present invention, the same refractive index change can be achieved with a much lower addition of Ta_2O_5 than can be achieved with GeO_2 .

15 Moreover, because tantalum is far less expensive than germanium, there is a significant cost savings resulting from the selection of tantalum as a dopant.

20 Another advantage is the high viscosity of Ta_2O_5 - SiO_2 glass, which is a function of the high melting point of tantalum. Ta_2O_5 has a melting point of 1887°C while SiO_2 and GeO_2 have melting points of 1715°C and 1116°C , respectively. Accordingly, the high viscosity of tantalum silicate glass makes the glass of the present invention a likely candidate for viscosity matching.

25 Additional advantages of the present invention are that tantalum oxide is chemically stable and insoluble in water, the thermal expansion of glass containing tantalum is lower than that of glass containing germanium, and the method of the present invention essentially eliminates crystallization within the Ta_2O_5 - SiO_2 containing glass during the manufacture of optical waveguides. The latter advantage results in improved optical characteristics.

30 Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the invention as described in the written description and claims hereof, as well as the appended drawings.

It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention and are intended to provide an overview or framework to understanding the nature and character of the invention as it is claimed.

5 The accompanying drawings are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiments of the invention, and together with the description serve to explain the principles and operation of the invention.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of an optical fiber manufactured in accordance with the present invention.

15 Fig. 2 is a cross-section view of the optical fiber of Fig. 1 taken through line 2-2 in Fig. 1.

Fig. 3 is a cross-section view of a Cl_2 reactor of the present invention.

Fig. 4 is a schematic view of a vapor delivery system shown forming a soot blank in accordance with the present invention.

20 Fig. 5 is a schematic view of a first preferred embodiment of a consolidation furnace of the present invention taken in cross-section.

Fig. 6 is a schematic view of a second preferred embodiment of a consolidation furnace of the present invention taken in cross-section.

25 Fig. 7 is a photomicrograph of a Ta_2O_5 doped core glass consolidated at 1450°C in a helium atmosphere.

Fig. 8 is a photomicrograph of a Ta_2O_5 doped core glass consolidated at 1450°C in a helium atmosphere.

Fig. 9 is a photomicrograph showing the core-clad interface of Ta_2O_5 doped glass consolidated at 1450°C in a helium atmosphere.

30 Fig. 10 is a photomicrograph of a Ta_2O_5 doped core glass consolidated at 1550°C in a helium atmosphere.

Fig. 11 is a photomicrograph of a Ta₂O₅ doped core glass consolidated at 1550°C in a helium atmosphere.

Fig. 12 is a photomicrograph of a Ta₂O₅ doped core glass consolidated at 1550°C in a helium atmosphere.

5 Fig. 13 is a photomicrograph of a Ta₂O₅ doped core glass consolidated at 1450°C in a vacuum atmosphere.

Fig. 14 is a photomicrograph of a Ta₂O₅ doped core glass consolidated at 1550°C in a vacuum atmosphere.

10 Fig. 15 is a photomicrograph of a Ta₂O₅ doped core glass consolidated at 1650°C in a vacuum atmosphere.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 The present invention expressly contemplates the manufacture of single-mode optical waveguide fibers, multimode optical waveguide fibers, and planar waveguides regardless of any specific description, drawings, or examples set out herein. In addition, it is anticipated that the present invention can be practiced in conjunction with any of the known optical waveguide processing techniques, including, but not limited to, the outside vapor
20 deposition (OVD) technique, the modified chemical vapor deposition (MCVD) technique, the vertical axial deposition (VAD) technique, the plasma chemical vapor deposition (PCVD) technique, and sol-gel techniques, to name a few. However, for the purposes of this specification, the tantala silicate soot and blanks described herein and shown in the accompanying drawing figures are
25 described as being manufactured using the OVD technique.

Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference characters will be used throughout the drawings to refer to the same or like parts. An
30 exemplary embodiment of the optical waveguide of the present invention is shown in Fig. 1, and is designated generally throughout by reference character 20.

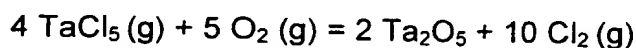
In accordance with the invention, the present invention for an optical waveguide fiber 20 includes a high purity glass cladding 22 and a high refractive index glass core 24 bonded by the cladding 22. As embodied herein, and depicted in Figs. 1 and 2, high purity glass cladding 22 is predominantly silica, and core 24 includes silica doped with tantalum in the desired proportions.

Optical waveguide fiber 20 having between about 2 to 5 wt% non-crystalline Ta₂O₅ after consolidation has been demonstrated to exhibit a loss of less than about 1.8 dB/km at 1550 nm. In a preferred embodiment, light attenuation in optical waveguide fiber 20 is less than 0.25 dB/km at 1550 nm.

A preferred embodiment of the method of manufacturing a low-loss optical waveguide having a high refractive index core includes the steps of forming a soot blank which includes Ta₂O₅ and SiO₂, consolidating the soot blank to form a cane under conditions suitable to prevent crystallization of the Ta₂O₅, and drawing the cane into an optical fiber. The Ta₂O₅ can be delivered using chemical vapor deposition techniques known in the art or via liquid delivery. The SiO₂ can similarly be delivered using known chemical vapor deposition techniques or liquid delivery.

An exemplary embodiment of a reactor for use with the chemical vapor deposition technique is shown in Fig. 3. Reactor 26 includes a diffuser 28, a preheat zone 30, and a reaction zone 32. In operation, fragments of tantalum 34 are packed within the preheat zone 30 of reactor 26 and chlorine (Cl₂) gas is flowed through diffuser 28 and over the fragments of tantalum 34 within reactor 26. Reactor 26 includes two separate heater coils (not shown) for the preheat zone 30 and reaction zone 32. When the heat in the reaction zone is 350°C or greater, a sufficient quantity of TaCl₅ gas is formed in reactor 26 to provide a desired amount of Ta₂O₅ in the soot.

As shown schematically in Fig. 4, TaCl₅ gas is delivered from vapor delivery system 36 to a burner assembly 38. The TaCl₅ is converted to Ta₂O₅ in the burner flame 40 according to the following reaction:



Finely divided amorphous Ta_2O_5 containing soot 42 is thereafter projected from the flame for capture and further processing. In a preferred embodiment, soot 42 is captured on a rotating mandrel 46 to form a soot blank 44. The amount of Ta_2O_5 captured on soot blank 44 is determined by the number of lateral passes made by burner assembly 38 along the length of soot blank 44, as well as the flow rate of Cl_2 through reactor 26.

The consolidation furnaces used for consolidating germania silicate blanks manufactured using OVD techniques typically provide temperatures of between 1000°C and 1450°C . Through experimentation, it has been found that such furnaces do not provide the heat necessary to perform the consolidation step without crystallization in the $\text{Ta}_2\text{O}_5\text{-SiO}_2$ containing glass as required for the present invention. Accordingly, improved consolidation furnaces capable of achieving temperatures in excess of 1450°C are needed for the present invention. The preferred embodiments of such consolidation furnaces are shown schematically in Figs. 5 and 6.

Fig. 5 depicts a first preferred embodiment of the consolidation step of the method of manufacturing a low loss optical waveguide having a high refractory index core. Soot blank 44 is held within consolidation furnace 48 where it is exposed to a gas 50. Gases such as, but not limited to, chlorine, helium, and oxygen, or combinations thereof, are delivered into consolidation furnace 48 to form the atmosphere 52 therein. Presently, the preferred gas, helium, is flowed across soot blank 44 while temperatures within consolidation furnace 48 are preferably elevated to 1600°C or greater. These conditions are maintained within consolidation furnace 48 until the $\text{Ta}_2\text{O}_5\text{-SiO}_2$ core glass temperatures are maintained at 1600°C or higher for a suitable time to sinter and vitrify the glass. After taking the additional processing steps commonly known to those skilled in the art in optical fiber manufacture, the resulting cane is drawn into an optical fiber. It is anticipated that an optical fiber manufactured from a SiO_2 soot blank containing 2 to 5 wt% Ta_2O_5 , and heat treated to a temperature of 1600°C or higher in a flowing helium atmosphere will have an attenuation of less than about 0.25 dB/km at 1550 nm. In a preferred embodiment, the temperature range is approximately 1600°C to 1700°C .

Fig. 6 depicts a second preferred embodiment of consolidation furnace 48 shown supporting soot blank 44. In this embodiment of the present invention, soot blank 44 is heated within a vacuum atmosphere. As used herein, the phrase "vacuum atmosphere" means an atmosphere less than atmospheric pressure. As depicted in Fig. 6, a pump 56 or other pressure-reducing device, removes the air from within consolidation furnace 48, thereby decreasing the pressure therein. As a result, soot blank 44 can be heat treated at temperatures lower than 1600°C to sinter and vitrify soot blank 44.

Typically, soot blank 44 is heated to a temperature between 1500°C and 1600°C in a vacuum atmosphere so that the Ta₂O₅-SiO₂ core glass temperatures reach between 1500°C and 1600°C for a sufficient time to result in clear glass which is substantially free of crystals. In a preferred embodiment, the vacuum atmosphere 54 within consolidation furnace 48, exhibits a pressure of less than about 10⁻⁴ torr. Following the additional processing steps commonly known to those skilled in the art of optical fiber manufacture, the resulting cane is drawn into an optical fiber. An optical fiber manufactured from a soot blank 44 containing SiO₂ and about 2 to 5 wt% Ta₂O₅, and heat treated at temperatures ranging between 1500°C and 1600°C in a vacuum atmosphere having a pressure of less than 10⁻⁴ torr is expected to exhibit attenuation of less than about 0.25 dB/km at 1550 nm.

A significant advantage of the method of the present invention is the crystalline free consolidation of Ta₂O₅ containing soot blanks. The following examples illustrate the effectiveness of the method of the present invention.

Example 1

A core blank was made by depositing 100 passes of Ta₂O₅-SiO₂ at an analyzed chemical wt% of 5.55 Ta₂O₅, followed by 177 passes of SiO₂. The resulting soot preform specimen was cut into cross-sectional slices approximately 25 millimeters long and approximately 50 to 60 millimeters in diameter. Samples were then fired at a temperature of 1450°C in flowing helium as shown in Figs. 7-9. The scanning electron micrographs (SEMs) of

the core material (Figs. 7 and 8) and the core material below the core-clad interface (Fig. 9) show that crystallization is prevalent in the Ta₂O₅-SiO₂ containing glass. As shown clearly in the fiber section 60 of FIG. 9, the silica cladding 62 is easily distinguished from the Ta₂O₅-SiO₂ containing core 64 as the cladding 62 has consolidated to a clear, amorphous glass. A core-clad interface region 66 is clearly visible between the cladding 62 and core 64.

Example 2

Additional slices of the soot preform specimen described above with respect to Example 1 were heated to 1550°C under a flowing helium atmosphere. The results of this experiment are shown in Figs. 10 and 11. The SEM's again show that the Ta₂O₅ containing core glass depicted in Figs. 10 and 11 contained numerous crystals. In fact, crystallization is so prevalent that increasing the temperature by approximately 100°C does not appear to reduce crystallization as compared to Example 1.

Example 3

An additional slice from the soot preform specimen described in Example 1 above was heat treated in a flowing helium atmosphere to a temperature of 1650°C. As shown in the SEM of Fig. 12, the core sample consolidated to a clear glass having no apparent crystallization.

Example 4

Additional slices of the soot preform specimen described in Example 1 were also fired at temperatures of 1450°C, 1550°C and 1650°C in a vacuum atmosphere of 1×10^{-4} torr. As seen in Fig. 13, the SEM shows that crystallization is present in the Ta₂O₅ containing core glass after heat treatment

at 1450°C. However, at treatment temperatures of 1550°C and 1650°C, as shown in the SEM's of Figs. 14 and 15, respectively, no crystallization occurs in the Ta₂O₅-SiO₂ core glass.

5 To permit other testing, single-mode step index optical fibers were drawn from other core blanks prepared in a manner substantially similar to that described above with respect to examples 1 – 4. The % Δ, and attenuation for fibers containing different amounts of Ta₂O₅ by weight percent are shown below in Table 1.

Table I

Results for Single Mode Fibers with Tantalum Silicate Core

Sample #	Wt%	Delta (%)	Attenuation	Attenuation	Attenuation
	Ta ₂ O ₅		@ 1310 nm	@ 1380 nm	@ 1550 nm
1	2.0	0.25	15.6	29.5	4.3
2	2.0	0.25	33.3	40.6	12.4
3	2.0	0.25	26.7	38.8	11.3
4	2.9	0.31	3.6	16.4	2.25
5	2.9	0.30	2.89	7.26	1.73
6	3.1	0.34	4.3	21.5	2.21
7	4.5	0.50	212.7	175.2	82.4

10 The consolidation furnace used to heat treat the fibers listed in Table I were standard furnaces commonly used to consolidate GeO₂-SiO₂ optical fiber preforms. Accordingly, the maximum temperature available for consolidation was 1450°C. Thus, the maximum temperature of 1450°C was used to

15 consolidate each of the core blanks listed in Table I above. The lowest loss attained was for the core blank having 2.9 wt% Ta₂O₅. At 1550 nm the attenuation was 1.73 dB/km. These results confirm the importance of using consolidation temperatures higher than 1450°C for Ta₂O₅-SiO₂ containing optical fibers. Based upon this information and the experiments described

20 above in Examples 1 through 4, it is anticipated that Ta₂O₅-SiO₂ containing optical fibers will exhibit losses of less than about 0.25 dB/km at 1550 nm when the soot blanks corresponding to these fibers are consolidated in consolidation furnaces capable of sustaining temperatures greater than 1500°C.

It will be apparent to those skilled in the art that modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. Thus it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

WE CLAIM:

1. A method of manufacturing a low loss optical waveguide having a high refractive index core, said method comprising the steps of:
 - 5 forming a soot blank comprising Ta_2O_5 and SiO_2 ;
 - consolidating said soot blank to form a cane under conditions suitable to prevent crystallization in said blank; and
 - drawing said blank into an optical fiber.
- 10 2. The method as claimed in claim 1 wherein the step of consolidating said soot blank comprises the steps of:
 - exposing said soot blank to an atmosphere comprising helium; and
 - heating said soot blank to a temperature greater than 1550°C .
- 15 3. The method as claimed in claim 1 wherein the step of consolidating said soot blank comprises the steps of:
 - exposing said soot blank to a vacuum atmosphere, and
 - heating said soot blank to a temperature greater than 1450°C .
- 20 4. The method as claimed in claim 3 wherein the vacuum atmosphere comprises a pressure of less than about 10^{-4} torr.
- 25 5. The method as claimed in claim 2 wherein the atmosphere comprises helium and oxygen.
6. The method as claimed in claim 1 wherein the step of forming a soot blank comprises the step of doping said soot blank with between about 2.5 wt% Ta_2O_5 to about 3.5 wt% Ta_2O_5 .
- 30 7. The method as claimed in claim 1 wherein said forming and consolidating steps comprise selecting parameters suitable to result in the optical fiber exhibiting a loss of less than about 1.8 dB/km at 1550 nm.

8. The method as claimed in claim 1 wherein said forming and consolidating steps comprise selecting parameters suitable to result in the optical fiber exhibiting a loss of approximately .25 dB/km at 1550 nm.

9. The method as claimed in claim 8 wherein the step of consolidating said soot blank comprises the steps of:

exposing said soot blank to an atmosphere comprising helium; and heating said soot blank to a temperature greater than 1550° C.

10. The method as claimed in claim 8 wherein the step of consolidating said soot blank comprises the steps of:

exposing said soot blank to a vacuum atmosphere; and heating said soot blank to a temperature greater than 1450° C.

11. The method as claimed in claim 1 further comprising the step of overcladding said blank to form a cladding comprising SiO₂.

12. The method as claimed in claim 1 wherein the step of forming said soot blank comprises the steps of:

flowing Cl₂ gas over Ta within a Cl₂ reactor at a temperature greater than 350° C to form TaCl₅;

delivering the TaCl₅ to an OVD burner to form soot comprising Ta₂O₅; and

depositing said soot on a rotating mandrel to form said soot blank.

13. An optical fiber made by the method of claim 1.

14. An optical fiber comprising;

a high purity glass cladding; and

a glass core bounded by said cladding, said glass core having a higher refractive index than said cladding, said glass core including between about 2-

5 wt% Ta₂O₅ after consolidation, and wherein light attenuation in said optical fiber is less than about 1.8 dB/km at 1550 nm.

5 15. The optical fiber as claimed in claim 14 wherein said glass core further includes SiO₂ and wherein said optical fiber is substantially free of crystals.

16. The optical fiber as claimed in claim 15 wherein light attenuation in said optical fiber comprises about 0.25 dB/km at 1550 nm.

10 17. A glass for use in the core of an optical waveguide comprising:
SiO₂; and

by weight on an oxide basis after consolidation, between about 2% non-crystallized Ta₂O₅ to 5% non-crystallized Ta₂O₅.

15 18. The glass as claimed in claim 17 wherein said core glass is consolidated in a helium atmosphere at a temperature of between about 1600° C to about 2000° C.

20 19. The glass as claimed in claim 18 wherein said core glass is consolidated in a helium atmosphere at a temperature of between about 1600° C to about 1800° C.

25 20. The glass as claimed in claim 19 wherein said core glass is consolidated in a helium atmosphere at a temperature of between about 1600° C to about 1650° C.

21. The core glass as claimed in claim 17 wherein said core glass is consolidated in a vacuum atmosphere at a temperature greater than about 1450° C.

22. The core glass as claimed in claim 17 wherein said core glass is bounded by a cladding comprising SiO_2 to form an optical fiber, and wherein light attenuation in said optical fiber is less than about 1.8 dB/km at 1550 nm.

5 23. The core glass as claimed in claim 22 wherein light attenuation in said optical fiber is less than 0.25 dB/km at 1550 nm.

FIG. 1

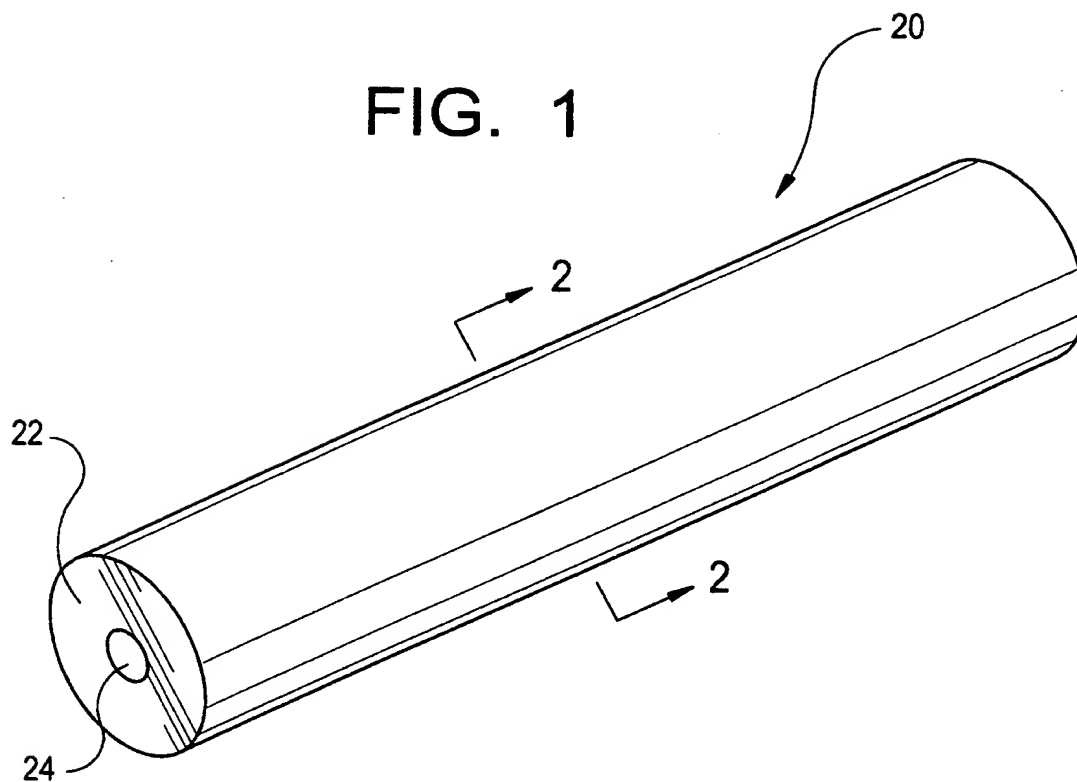


FIG. 2

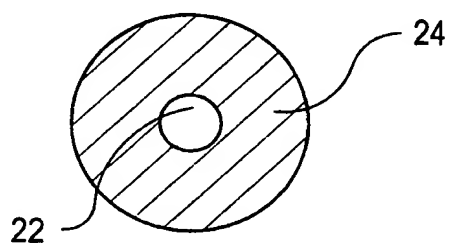


FIG. 3

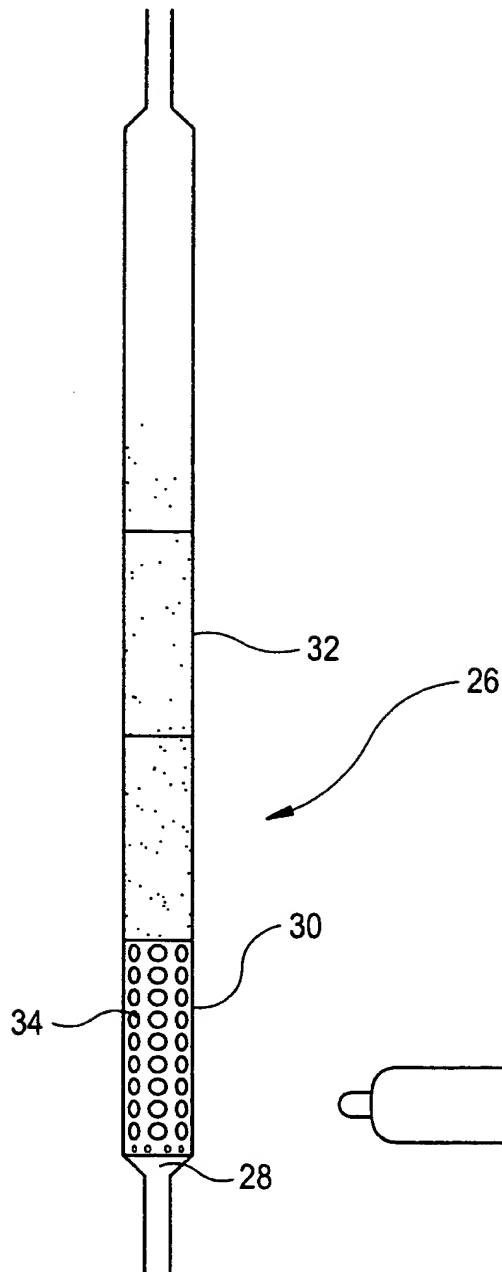


FIG. 4

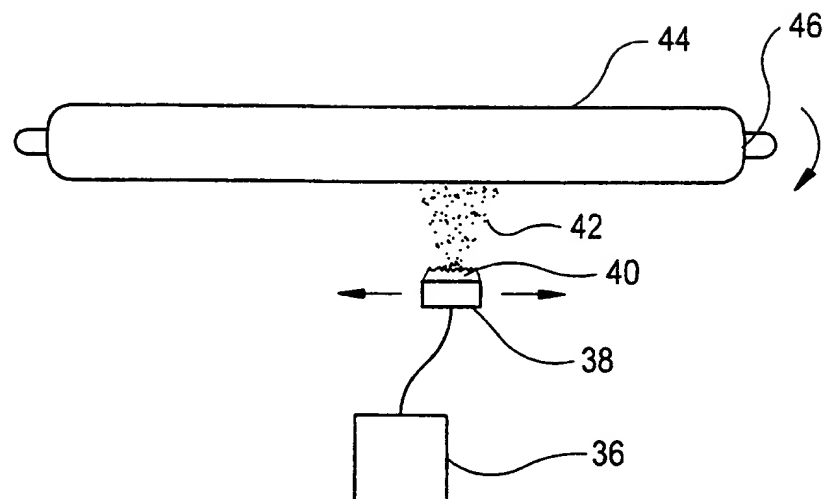


FIG. 5

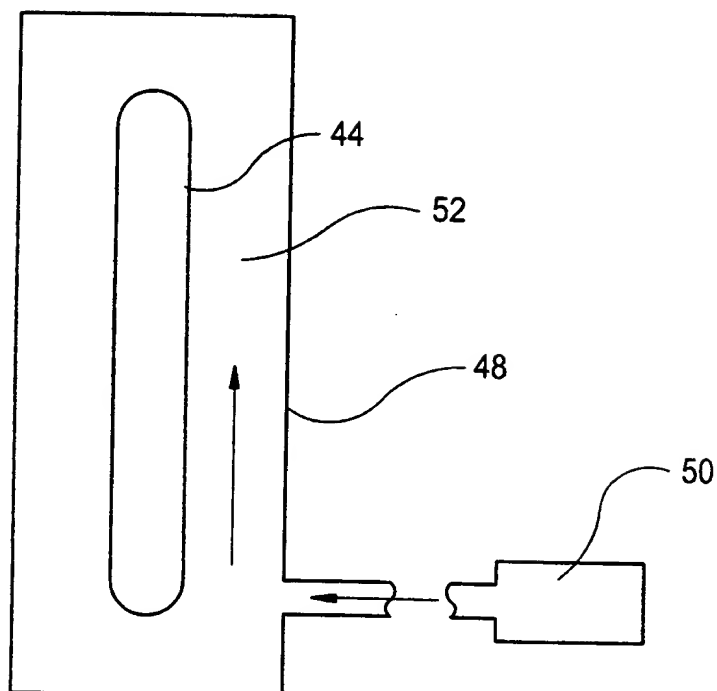


FIG. 6

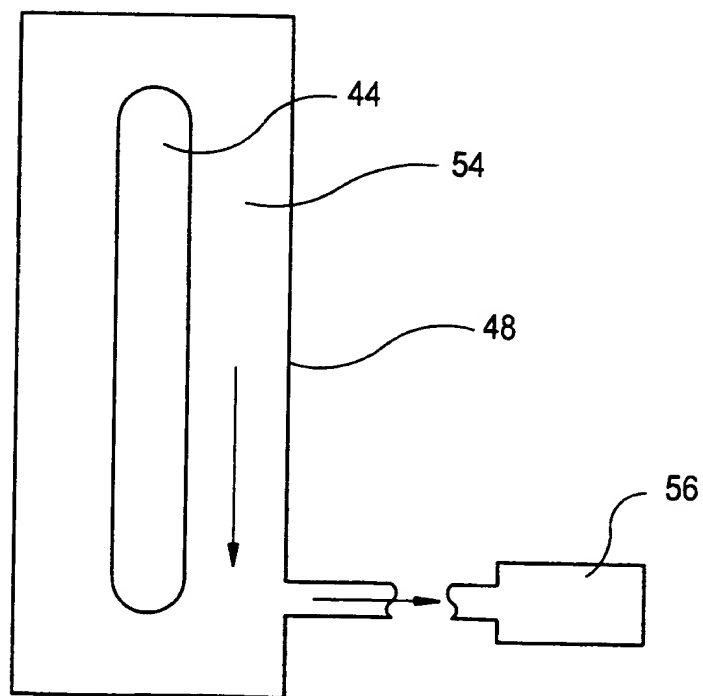


FIG. 7

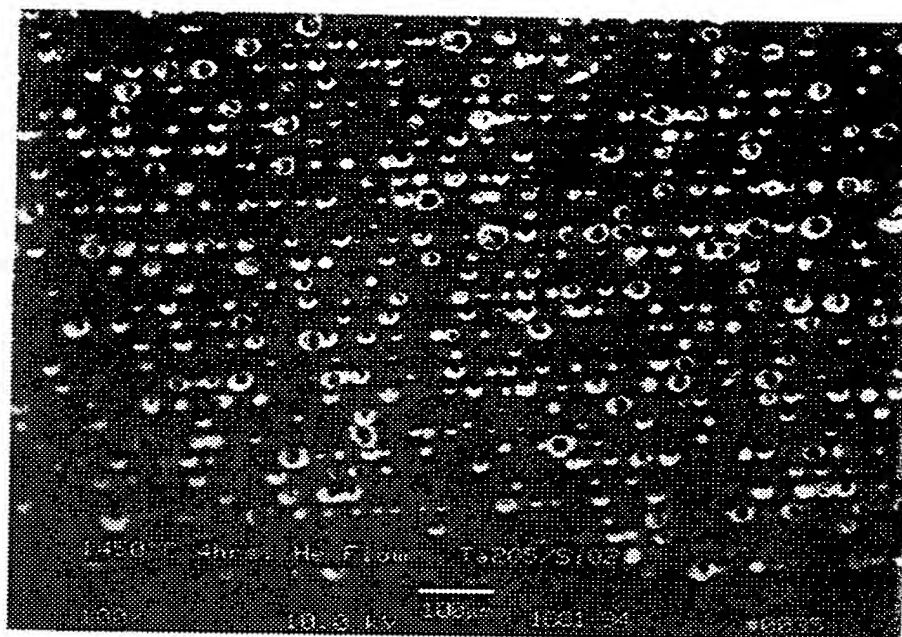


FIG. 8

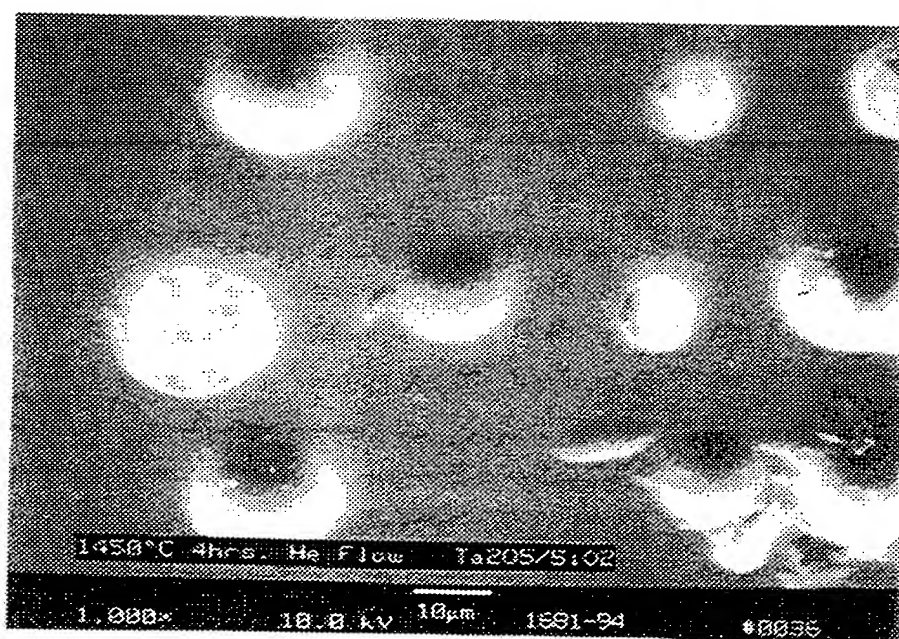


FIG. 9

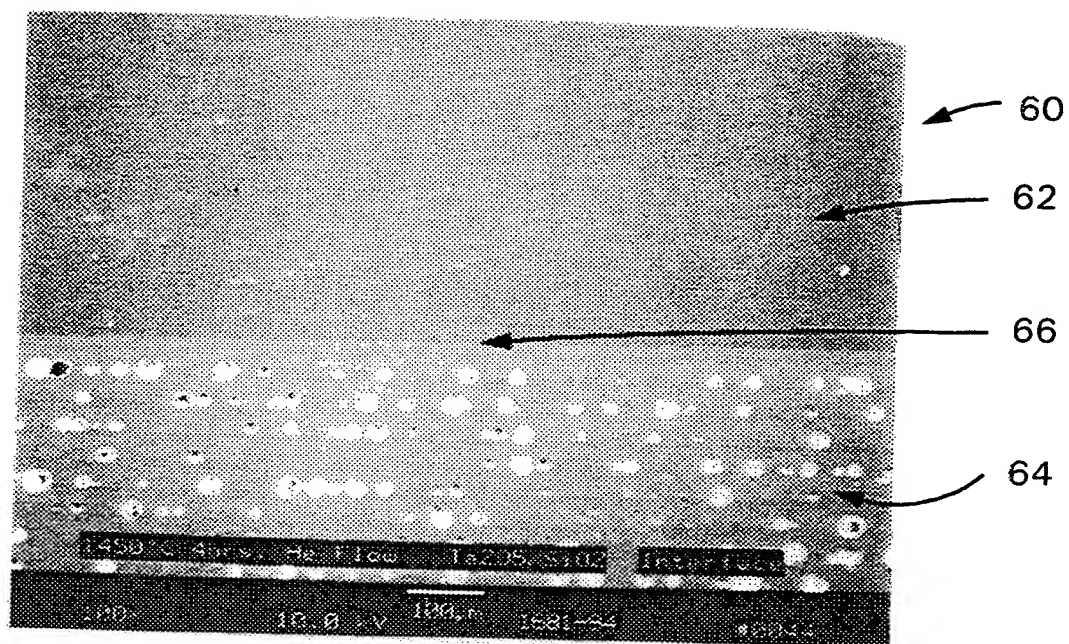


FIG. 10

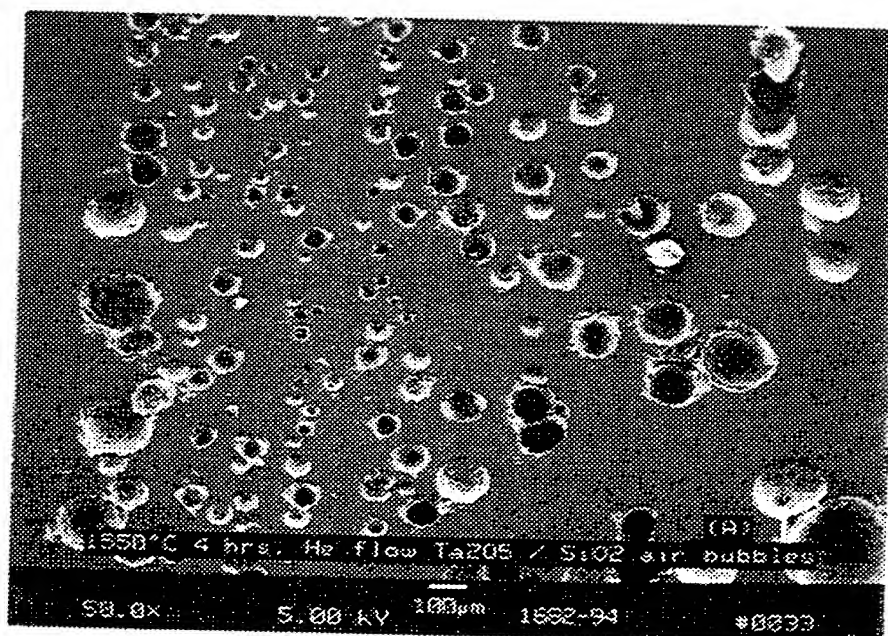


FIG. 11

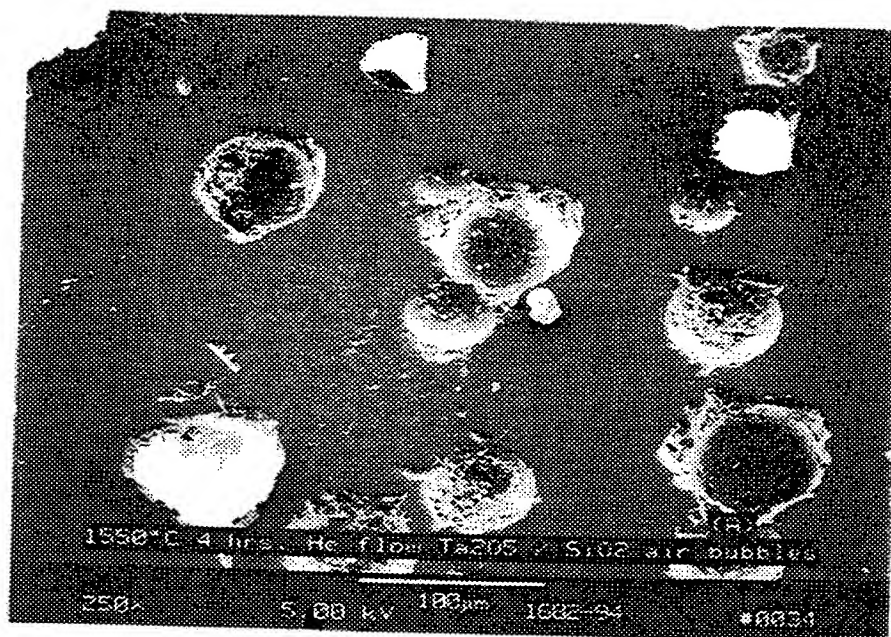


FIG. 12

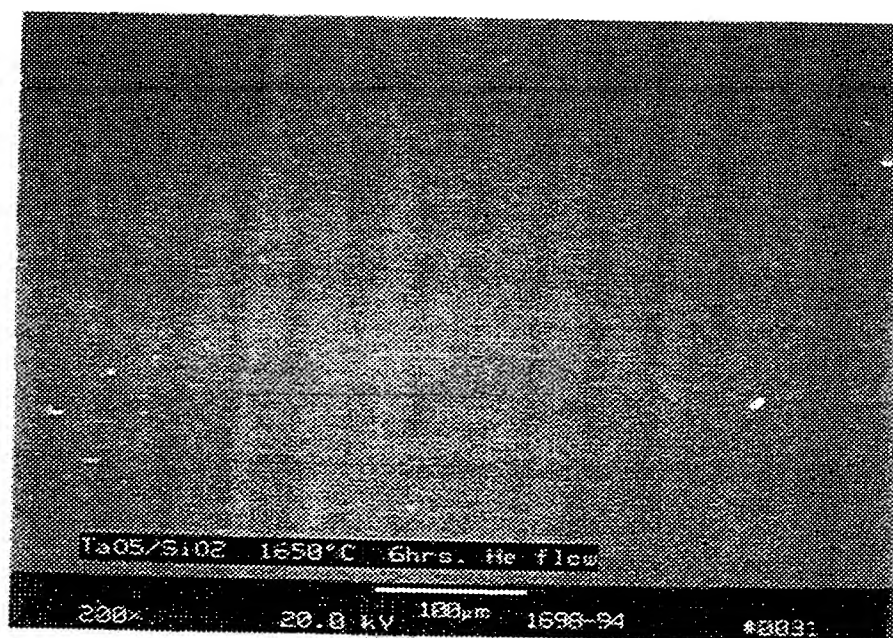


FIG. 13

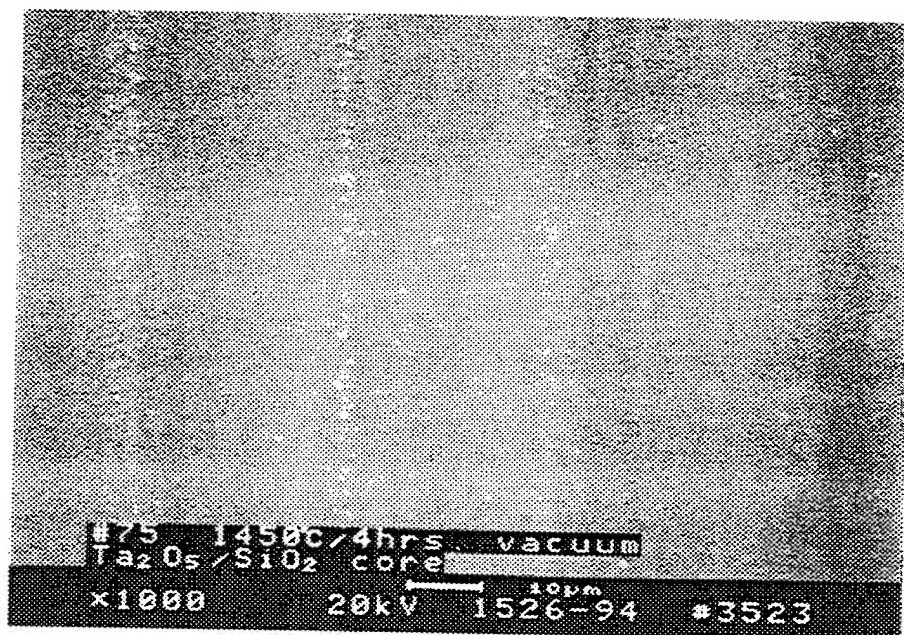
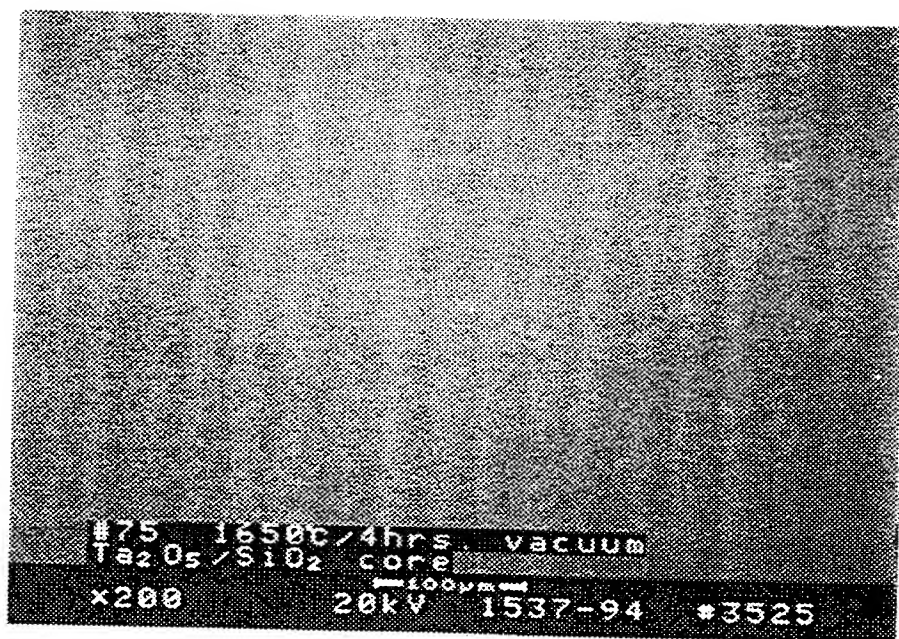


FIG. 14



FIG. 15





INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷: C03B 37/014, 13/04, C03C 3/06, 13/04	A3	(11) International Publication Number: WO 00/39039 (43) International Publication Date: 6 July 2000 (06.07.00)
(21) International Application Number: PCT/US99/29225 (22) International Filing Date: 9 December 1999 (09.12.99) (30) Priority Data: 60/114,369 30 December 1998 (30.12.98) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; One Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): DELISO, Evelyn, M. [US/US]; 248 Chemung Street, Corning, NY 14830 (US). MARLATT, Deborah, L. [US/US]; 898 County Route 85, Addison, NY 14801 (US). PIERSON, Michelle, D. [US/US]; 678 Beartown Road, Painted Post, NY 14870 (US). TENNENT, Christine, L. [US/US]; 4748 Clawson Drive, Campbell, NY 14821 (US). (74) Agent: CHERVENAK, William, J.; Corning Incorporated, Patent Dept., SP TI 3-1, Corning, NY 14831 (US).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> (88) Date of publication of the international search report: 9 November 2000 (09.11.00)	
(54) Title: TANTALA DOPED OPTICAL WAVEGUIDE AND METHOD OF MANUFACTURE		
(57) Abstract <p>The present invention is directed to low loss optical waveguides doped with tantala and methods for manufacturing such waveguides. SiO₂ soot is doped with Ta₂O₅ to form a soot blank which is consolidated under conditions suitable to prevent the crystallization within the Ta₂O₅-SiO₂ containing waveguides. The resulting cane is then either drawn into an optical fiber or overclad and subsequently drawn into an optical fiber. High temperature consolidation in either a gaseous atmosphere or vacuum atmosphere is used to sinter and vitrify the soot blank prior to drawing to produce a low loss optical waveguide fiber.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

International Application No.

PC 99/29225

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03B37/014 C03B13/04 C03C3/06 C03C13/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 06 Derwent Publications Ltd., London, GB; Class L01, AN 1985-034244 XP002141764 & JP 59 227740 A (HITACHI CABLE LTD.), 21 December 1984 (1984-12-21) abstract ---	1,6-8, 13-17, 22,23
X	US 3 785 722 A (P.C.SCHULTZ) 15 January 1974 (1974-01-15)	17
A	column 4, line 5 - line 10; examples A,H ---	1,13,14, 22
A	US 3 659 915 A (R.D.MAURER ET AL.) 2 May 1972 (1972-05-02) claims 1,4 ---	1,13,14, 17,22
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 July 2000

Date of mailing of the international search report

13/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Stroud, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29225

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 806 570 A (J.S.FLAMENBAUM ET AL.) 23 April 1974 (1974-04-23) column 7, line 35 - line 39; claim 12; figure 5 -----	1,12-14, 17,22
A	DATABASE WPI Section Ch, Week 06 Derwent Publications Ltd., London, GB; Class L01, AN 1985-034245 XP002141765 & JP 59 227741 A (HITACHI CABLE LTD.), 21 December 1984 (1984-12-21) abstract -----	1,13,14, 17,22
A	FR 2 333 628 A (P.VERGNON ET AL.) 1 July 1977 (1977-07-01) claims 1,2 -----	1,13,14, 17,22
A	WO 86 04573 A (AT&T CO.) 14 August 1986 (1986-08-14) page 13, line 12 - line 32 page 16, line 4 - line 7 -----	1,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29225

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 59227740	A	21-12-1984	NONE	
US 3785722	A	15-01-1974	NONE	
US 3659915	A	02-05-1972	BE 766972 A	10-11-1971
			CA 951555 A	23-07-1974
			DE 2122896 A	16-12-1971
			FR 2088485 A	07-01-1972
			GB 1322992 A	11-07-1973
			NL 7106383 A	15-11-1971
US 3806570	A	23-04-1974	CA 1025735 A	07-02-1978
			DE 2313249 A	11-10-1973
			FR 2178177 A	09-11-1973
			GB 1430681 A	31-03-1976
			GB 1430682 A	31-03-1976
			JP 49009523 A	28-01-1974
			NL 7304382 A, B,	02-10-1973
JP 59227741	A	21-12-1984	NONE	
FR 2333628	A	01-07-1977	NONE	
WO 8604573	A	14-08-1986	US 4666247 A	19-05-1987
			CA 1274127 A	18-09-1990
			DE 3685099 A	04-06-1992
			EP 0225884 A	24-06-1987
			JP 4075857 B	02-12-1992
			JP 62501699 T	09-07-1987